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(54) Cementitious coatings

(57) A flexible protective cementitious coating comprises a hydraulic cement, a mineral aggregate such as sands and gravels or crushed ores, admixtures and a polymeric water based emulsion such as latex polymer and provides a physical and chemically resistant coating for engineering substrates. The density coating of the composition can be controlled to suit the application, and the coating has particular use for providing impact protection to steel pipelines laid by the "reel barge" method and others, or as a lightweight resilient insulating coating. The resilience of the coating is suitable for use as a vehicle underbody seal, and protection to backfilled underground structures.

The coating comprises less than 20% w/w of hydraulic cement and has a polymer solid to cement ratio of greater than 1.0.

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CEMENTITIOUS COATINGS

This invention relates to a range of cementitious compositions which could, depending on aggregate type, be described as mortars or concretes but which are flexible and protective, and their uses.

Conventional mortars and concretes are very well known for a vast range of civil engineering and constructional applications. They are, however, unsuited to many applications where flexibility, enhanced bonding or resilience are required. These properties can be increased by incorporating one or other of a number of polymer admixtures. However, to date, the success of doing this has been limited because the setting behaviour and strength development of such compositions are generally adversely affected to the point that their usefulness is lost.

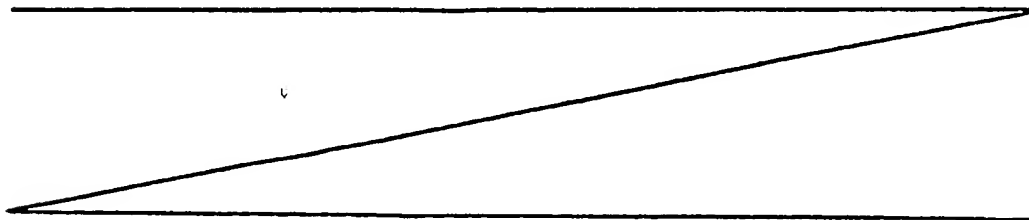
Specifically, the uses of known mortars and concretes have been very limited, for example to applications where thin protective coatings have been required, and they have proven unsuited to pipe-coating applications in the "reel barge" method because of their brittleness. They are unable to withstand the high bending strains and significant impact forces applied to pipe laid down by the "reel barge" method (A.C. Palmer (Ref.1)) and have shown no

advantage as the basis of weight coatings to reduce the amount of, for example, steel needed to be used in the pipe composition.

Polymer-modified thin cement coatings for pipelines have been available since the early 1980's including a system called FRC 80 (Palmer q.v.) which was developed for use in applications where on-shore transportation (e.g. by road or train) of fusion-bonded epoxy-coated pipes to a concrete coating plant could cause damage to the epoxide protective layer. This type of coating needed to provide protection using the minimum thickness possible, in order that the eventual weight coating could be as thick as possible.

A similar system for pipe protection was developed by Evode (3). The use of these types of materials was never envisaged as a final coating nor for "reel barge" applications. They could only withstand limited bending strains before the fibre carrier or matting would shear.

For example, the Evode system referred to above has been used since the early 1980's to provide a relatively



thin protective coating for on-shore transportation of pipes and for protection during on-shore pipe laying (4). However, this type of technology requires a fibre-mesh reinforcement/carrier in order to work successfully, but this carrier has a tendency to cause the coating to delaminate under the bending strains imposed by the "reeled pipes" (5). Another draw-back for off-shore use is the low density of the final set composition at 1.8-1.9 Kg³/M³. This density is much too low for this type of system to provide an effective weight coating at practical thicknesses employed.

Up to the time of the present invention, no system has combined sufficient flexibility and durability, at a density and cost which permits its economical use as a protective weight coating for reeled pipes.

Various difficulties had to be addressed in trying to find a solution to the overall problem which included:

Polymer-modified cementitious compositions will, on water-soaking, stiffen considerably, if the cement component is left largely unhydrated by the setting process. In the case of a pipe coating, some stiffening once the pipe is in place may be desirable to increase the rigidity of the pipe, but it is most undesirable prior to laying the pipe, because it could lead to the coating becoming damaged by the bending strains. To overcome this

problem, the composition needs to have a sufficiently high water/cement ratio so that nearly all the cement is hydrated early in the process and coating life to give predictable, consistent stiffness. An example of this type of consideration is that, to completely hydrate pure mono-calcium aluminate (principal component of high alumina cement), the water:mono-calcium aluminate ratio should be just above 1.

Furthermore, currently available systems that do not contain more than 20% polymer by total weight of the final set composition also contain a high cement content because they are designed to act as thin adhesive coatings or "bond coats" to promote bonding between substrate and concrete or mortar coatings (see table 1). They are not suitable for the production of an independent flexible body (Ref. 16, 17, 18 and 19).

These compositions incorporate sufficient polymer into the matrix by using water-based emulsions, e.g. natural rubber lattices; styrene butadiene (SBR); styrene acrylate lattices; and polyvinyl acrylates (PVA) of which the latter are not water resistant.

The maximum polymer contents of these emulsions is of the order of 50% and therefore to maximise flexibility and satisfy the requirement for the water:cement ratio above, the emulsion:cement ratio must be about twice that of the

water:cement ratio (depending on the composition of the components).

The cement component is the active part of the composition, therefore the inorganic part of the composition must contain sufficient cementitious material to provide adequate strength development. However, the disadvantage of gaining strength development through increased cement content is that this subsequently requires addition of increasing quantities of expensive polymer, as an emulsion, in order to ensure the complete hydration of the cement and to maintain initial flexibility of the system over the rapidly-stiffening cement matrix.

In practice, most flexible systems use a conventional cement content ranging from 15-35% (Ref. 15) and use insufficient emulsion, therefore leaving residual unhydrated cement, which can hydrate on soaking.

These compositions could give the required flexibility but they contain too much cement, are slow setting and produce densities which are too low for weight coating applications because their "filling capacity" with aggregates is too low. The rheology of the subsequent mixture is not suited for building up a layer which will remain stable until the set has occurred.

The pipe coating industry has focused on the classic indicators of cement properties, i.e. those which denote a rather brittle material such as concrete rather than a durable protective weight coating material, which can withstand the rigours of pipe laying and subsequent impacts from trawl boards, etc.

High density is an important property for any composition destined for use as a weight coating for off-shore pipelines, such as "reeled pipes". The established coatings contained too much low density material, such as polymer, so that there is little scope for these to be used as a weight coating.

Thus, the present inventors were informed that an adequate coating had still not been developed, and this was limiting the applicability of reeled pipes. We considered the difficulties outlined above and decided to look at a completely new approach to the problem where we would minimise the cement content in order that a good level of permanent flexibility could be achieved and maintained, whilst permitting the inclusion of more dense aggregate.

The present invention therefore provides:
a cementitious coating composition which comprises
(a) less than 20% w/w of the composition of a hydraulic cement;

- (b) more than 40% w/w of a mineral aggregate, substantially inert with respect to the hydraulic cement;
- (c) a polymeric water-based emulsion which is stable at pH>10 in an amount whereby the polymer content of the composition, once set, is greater than 16%; and
- (d) a setting control composition suitable for setting the hydraulic cement.

According to the present invention there is provided a flexible protective cementitious coating composition of enhanced properties extending the possible applications of cement based mortars and concretes for a wide range of coating applications. It does not require the use of a fibre-mesh reinforcement and it can withstand the bending strains imposed by the "reel barge" type application of off-shore pipelines. This is at a density and cost which may facilitate more economical use of reeled pipes.

The hydraulic cement component (a) may comprise, for example, Portland cement, calcium aluminate or high alumina cement, or the like. The component described herein as 'cement' does not include cementitious blends which may include the cements mentioned above as essential components. The invented composition has a lower cement content than other comparable or related materials. Preferably, component (a) is present as less than 14% w/w of the composition, although it can be present

in the range of from 5-20% w/w.

The mineral aggregate can be an inorganic or synthetic mineral aggregate such as a high density crushed ore (e.g. iron ore or baryte); a natural sand or gravel; or synthetic high aspect ratio fibres.

The polymer in the water-based emulsion may be a synthetic latex or blend of styrene acrylates. The polymer content of the composition is high compared to that in known, related compositions. It is principally provided by means of a concentrated water-based polymer emulsion component. Preferably, the polymer comprises at least 6-8% w/w of the composition; more preferably it will comprise at least 16% w/w. These values do not include any polymer fibres or aggregates, e.g. rubber crumb which may also be added. These values compare with a maximum of approximately 10% quoted for the Evode system (Ref. 3).

The cement component is preferably made up into a fines component incorporating fillers and admixtures, which would solidify satisfactorily by hydraulic setting when mixed with at least equal amounts of the polymeric emulsion. It was found that the use of high alumina cement extended by limestone filler and/or ground granulated blast furnace slag, were particularly suitable, in that these showed slow reactions with the cements which could lead to better long term durability (Refs. 8 and 10). Other

compositions containing Portland cements were also found to give suitable properties but these were much slower to set.

The present invention therefore has a final set composition with a low cement content and a high polymeric content with a ratio of polymer solid:cement of greater than 1, but typically more than 1.5. This is higher than hitherto-known cementitious coating compositions wherein the ratio of polymer solids:cement in the final composition ranges up to 0.8.

The setting behaviour of the compositions of the invention may be adjusted in various ways including by the use of temperature and admixtures. The precise manner of this control depends on the composition of the cementitious component. The blends containing high alumina cements and ground granulated blast furnace slag (GGBFS) mixed with styrene acrylates and/or SBR's were found to have particularly suitable rheology and setting behaviour which could be modified by a range of admixtures known to be effective for high alumina cement, e.g. lithium salts as effective accelerators.

These blends were found to be very tolerant of different types and amounts of aggregates. These compositions permitted a higher level of aggregate addition

of various densities, whilst maintaining flexibility. In particular it was found that sands, barytes and crushed iron ore would permit the use of more polymer emulsion, whilst maintaining suitable rheological characteristics. These compositions permitted a higher level of aggregate additions of various densities, whilst maintaining flexibility. This would permit a wide range of potential densities depending on the type of application, ranging from 1.25 to 4.3 g/cm³, preferably up to about 2.85 g/cm³. It was also found that the setting of these compositions could be greatly accelerated by temperature, and even thermo-set in contact with a hot surface with rapid setting following in the interior of the composition. The compositions according to this invention may set hydraulically in adiabatical conditions at 20°C to provide touch dry surfaces within about 24 hours or less.

The compositions were found to be of low strength in conventional terms, i.e. low compressive strength, tensile and flexural strength, but elastic properties were found to exceed those of other cementitious pipe coating materials. The elastic properties of these compositions therefore made these superior materials for weight coating of reeled pipes. Within the specified parameters, these compositions can be varied by methods known to those skilled in the art to provide the optimum characteristics for applications for

which it is destined in terms of rheological application characteristics, flexibility, resilience, permeability, adhesion, development of Young's modulus, density and chemical resistance.

The flexible cementitious compositions of this invention may be applied by casting, spraying, wrapping or pouring. They can also be preformed into sheets or other required shapes ready for application.

These compositions are suitable for a wide range of applications including the following:

impact-resistant floor coverings; anti-static floor coverings; coatings for ship decks; underbody sealing of vehicles; protective coatings against corrosive salts and impact from backfill for below-ground structures; protective coatings to steel, concrete, epoxide and coal tar coatings; as a replacement for epoxide and coal tar coatings; as a fire inhibiting coating; and, in particular, to provide a flexible protective weight coating to steel pipe laid by the "reel barge" method.

EXAMPLE

COMPONENT	% OF WHOLE SET COMPOSITION
SOLIDS	
High alumina cement to BS915	7.05
Ground granulated blast furnace slag (GGBFS)	8.34
Sand	23.44
Crushed iron ore	23.44
Lithium carbonate	0.03
Proprietary hydroxy ethyl cellulose	0.20
POLYMER EMULSION TOTAL	
Styrene acrylate copolymer emulsion solids in suspension	37.5

TABLE 1

USES / COMPONENTS	CEMENT CONVENTIONAL		POLYMER MODIFIED MORTAR eg Floor Toppings Screeds Renderers, etc.	ADHESIVE BOND COAT eg Tack coat	"FLEXIBLE PROTECTIVE CEMENTITIOUS CONCRETE"	
	MORTAR	CONCRETE			NORMAL DENSITY	HIGH DENSITY
Cement	1	1	1	1	1	1
Water	0.35	0.45	0.3	0.25	0.3	0.3
Polymer Solids	-	-	0.1	0.25	1.6	1.6
Aggregate	Up to 3	Up to 6	Up to 3		7	Up to 11

All figures refer to parts by weight

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CLAIMS

1 A cementitious coating which sets hydraulically in less than 18 hours applied at thickness from 1mm to 150mm, comprising a hydraulic cement, fillers, aggregate, admixtures, and water dispersible polymer latex, where the polymer solid to hydraulic cement ratio is greater than 1.0 whilst the cement content of the final mix is maintained at less than 14% by weight, with an aggregate and filler to hydraulic cement ratio of greater than five to one by volume, which permits a repeatable strain of greater than 4% in the hardened compound.

2 A cementitious coating as claimed in Claim 1, where the water dispersible polymer latex is substantially based on acrylonitrile, styrene butadiene or styrene acrylate copolymer emulsions which are set to support the matrix during coating application by a combination of acceleration of the hydraulic cement by admixtures and heat by control of the temperature of raw materials and the substrate in ambient conditions from -5°C to 80°C .

3 A cementitious coating as claimed in Claim 1 and Claim 2 wherein the aggregate grading is adapted to provide a rheology suitable for the mixing and placing technique, which can include spraying, pouring, casting, wrapping or trowel application for the required coating thickness, and to maintain flexibility in the hardened state.

4 A cementitious coating as claimed in any preceeding claim where the selection of aggregates is adapted to provide the specified density for the hardened coating, and where entrained air may be adapted to act as a lightweight aggregate when introduced during mixing.

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Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
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Relevant Technical Fields

- (i) UK Cl (Ed.N) C1H (HAS, HAX, HCE, HCF, HCW, HXE)
 (ii) Int Cl (Ed.6) C04B 24/26, 28/02, 28/04, 28/06

Search Examiner
 MISS M KELMAN

Date of completion of Search
 5 JULY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
 1 TO 4

(ii) ONLINE: CHEMLIT, PATENTS

Categories of documents

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| <p>X: Document indicating lack of novelty or of inventive step.</p> <p>Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p>A: Document indicating technological background and/or state of the art.</p> | <p>P: Document published on or after the declared priority date but before the filing date of the present application.</p> <p>E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p>&: Member of the same patent family; corresponding document.</p> |
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Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1317603 A (DU PONT) See page 2 lines 40 to 71 and 90 to 102 and the Examples.	1 to 4
X	EP 0460744 A1 (C-CURE CHEMICAL) See the claims and Examples 1, 6 and 7.	1 to 4
X	US 5185389 A (GEM ENG) See Table B and column 4, lines 25 to 45.	1 to 4
X	US 3917771 A (BASILE) See column 2, lines 24 to 28 and 32 to 54.	1 to 4

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).